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Investigating the content of microplastics and other extraneous particles in Polish bottled water

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Abstract: Bottled water has enjoyed a global increase in popularity since it is generally perceived to be superior in quality to tap water and necessary when tap water is non-potable. As a result, ensuring that it meets the requisite quality standards is of vital importance. This work aims to examine the content of solid particles, including microplastics, in bottled water available in Polish stores. The second aspect is the preliminary determination of the influence of the water gassing process, together with thermal and light factors, on the content of particles in the water. The number of particles was counted by colour and shape, with the number ranging from 87 to 188 per litre of water; on average, there were 136 ±32 particles per litre of water, demonstrating that water from disposable plastic bottles is contaminated with various substances. The difference in the number of particles may be due to the origin of the waters, the processes they were subjected to prior to bottling, the properties of the bottles as packaging, and the conditions and length of storage and transport. Additional Fourier-transform infrared spectroscopy (FT-IR) analysis confirmed that about 75% of the particles were polymers, and 50% of them were plastics. Particularly alarming is the fact that the bottled waters mostly contained microplastic particles (MP) of smaller sizes, the kind which is recognized as being the most dangerous to human health. In the study, most particles were in the form of irregular shapes, which may indicate that they come from the destruction of waste or plastic products. This is also indicated by the domination of colourless particles. More particles were found in waters exposed to high and low temperatures than in waters stored at room temperature, potentially indicating that storage conditions for drinking water are important. Taking into account the results obtained, increasing attention should be paid to the health risks posed by such microplastics and there is a clear need to introduce legal regulations on the matter. The lack of any legal guidelines or unified standards in the field of MP research means that the results are not always representative, and it also makes it difficult to compare the results from different studies.

Keywords: plastic bottles, drinking water, solid particles, polymers, microplastics, FT-IR spectroscopy

INTRODUCTION

Plastics are a wide range of artificial materials that do not occur naturally, most often produced from petroleum or natural gas via the process of polymerization. Chemically, they are synthetic organic polymers that form different types of plastics depending on the chain length and composition

(Ouellette & Raw 2015). Plastics are distinguished by the fact that they are both light and durable, inert, resistant to corrosion, flexible, can be formed into any shape, and are cheap to produce. After the addition of appropriate modifying additives, their thermal stability increases, the burning rate decreases, or they acquire antistatic properties. Due to these features, plastics have been used in almost every area of life since the 1950s, e.g. as packaging, toys, and clothes. In some cases, they have displaced other products, e.g. glass and wooden packaging, while in others they have enabled new, better solutions, e.g. in medicine, space vehicles, and new technologies (Hopewell et al. 2009).

Plastics are a material obtained by combining monomers into polymer chains with the use of chemical additives that change the physicochemical properties of polymers without changing their structure. The most common additives are dyes, stabilizers, plasticizers, fillers, improvers, and flame retardants. Depending on what and how many monomers have been combined, the resulting plastics differ in properties which depend on the purpose for which they were produced (WHO 2019, Myszograj 2020). There are two general groups of plastics: thermoplastics and thermosetting plastics (duroplastics). Thermoplastics soften when heated, allowing them to be moulded, and then harden when cooled. This process can be repeated many times, which makes it possible to recycle them. Thermosetting polymers undergo chemical transformations when heated and permanent chemical bonds are formed between the polymer chains (WHO 2019).

The production of plastics in 1950 amounted to 2 million tonnes and annually thereafter. In 2019, it reached 368 million tonnes worldwide, of which 58 million tonnes, or 16%, were in Europe, and 51% in Asia (31% in China alone). In 2021, global plastic production increased by 4% to more than 390 million tonnes, demonstrating that there is an ongoing demand for plastics (PlasticsEurope 2022). The sectors in which the most plastics were used (in 2019) were packaging, 40%, and construction, 20%. Polyethylene terephthalate (PET), among all types of polymers, accounts for 8% of production (PlasticsEurope 2020). It is the most commonly used material for bottles, while polypropylene (PP) and polyethylene (PE) are the most commonly used for caps (WHO 2019). Approximately 57 billion PET plastic bottles are used annually in the EU, of which 2.4 billion are in Poland. A consequence of this has been a large amount of plastic waste which is frequently illegally dumped, abandoned, incinerated, or mishandled by users. As a result, plastics get into the water and air, being transported over long distances and shredded into millimetre sized particles or smaller (Hale et al. 2020).

A very important aspect when examining plastic particles is their size. Particles smaller than 5 mm are commonly referred to as microplastics (MP). Nanoplastics are generally defined as particles smaller than or equal to 100 nm while the terms meso-, macro-, and megaplastics are used to describe larger particles (Besseling et al. 2019). Microplastics are divided into primary and secondary types according to their source of origin. Primary MP is deliberately produced in microscopic sizes as a raw material for the plastics, pharmaceutical, or cosmetics industries (Wang et al. 2019). The largest source of primary MP in the environment is the use of polyester and acrylic fibres for the production of fabrics or coating fabrics with a thin layer of plastic. The share of man-made fibres in primary MP is as much as 35% (Boucher & Friot 2017). The next large sources are the abrasion of car tires while driving (28%) and city dust (24%). Fine plastic particles, added in the form of microbeads to cosmetics (e.g. toothpaste, scrubs, shampoos, eye shadows) and cleaning agents, account for only 2% of all virgin MP (Boucher & Friot 2017, Fiore et al. 2022, Zhou et al. 2023).

Secondary MP is formed as a result of the disintegration of larger plastic waste, which undergoes various physical, chemical, and biological processes, losing its original compactness, colour, or shape. In addition to plastic waste resulting from the common activities of people on land, MP is also made of ropes, nets, and other abandoned waste (whether accidentally or deliberately) during commercial fishing in the seas and oceans (Osman et al. 2023). Secondary microplastics account for 69% to 81% of the total MP in the marine environment (Munoz-Pineiro 2018). The impact of physical, chemical, and biological factors causes the gradual disintegration of large plastic elements. Physical factors include transport, sedimentation, and

accumulation, while chemical factors include degradation and adsorption, and biological factors include ingestion, transport, and digestion. Chemical degradation of plastics occurs under the influence of heat, UV radiation, oxidation, and chemical reagents. There is a decrease in the molecular weight of the polymer, which crumbles and breaks into smaller pieces visible to the naked eye or that are so small that a microscope is needed to observe them (Zhang et al. 2021).

Plastic particles can have different shapes and colours. Among the shapes characteristic of MP, there are (in descending order of appearance): asymmetric fragments, fibres, films, foams, pellets, balls, veins, beads, flakes, leaves, granules, foils, and nurdles (balls). Microplastics, just like plastics, can be colourless or coloured (Dahl et al. 2021, D'Hont et al. 2021). The colour of MP is largely blue (Kosuth et al. 2018, Kutralam-Muniasamy et al. 2020).

The quality of tap water in most countries is constantly being monitored and improved, but many people feel an aversion to such water due to its quality in the 20th century, when the level of water quality control and the condition of water supply systems was much worse than today. Bottled water is still required in some regions of the world where tap water is unsafe to drink and it is estimated that the deficit of good quality water may increase in the future. Bottled water has grown in popularity in many regions where it is generally perceived to be superior to tap water in many ways, including taste, quality, and convenience (Doria 2006, Saylor et al. 2011, Diduch et al. 2013, Salazar-Beltrán et al. 2018, Zhou et al. 2021). In Poland, water in plastic bottles began to be sold as mineral or spring water in the 1990s. This increased the demand for bottled water, hence the emergence of new entrepreneurs dealing with its distribution.

The presence of MP in waters was confirmed many years ago (e.g. Thompson et al. 2004, Browne et al. 2011, Cole et al. 2011). Plastic particles also began to be detected in many other components of the environment, and interest in the topic of microplastics has been growing year on year. Unfortunately, MP have also been found in various sources of drinking water, namely tap water (e.g. Kosuth et al. 2018, Koelmans et. al. 2019, Danopoulos et al. 2020, Lam et al. 2020, Kirstein et al. 2021, Gambino et al. 2022) or groundwater (e.g. Połeć et al. 2018, Mintenig et al. 2019, Singh & Bhagwat 2022, Viaroli et al. 2022). Checks on its presence in bottled water have also been conducted, but this research began relatively recently (4–5 years ago), with one of the first being Oβmann et al. (2018) and Schymanski et al. (2018). Others who dealt with this topic referred to their results (Mason et al. 2018, Koelmans et al. 2019) or compared them (Welle & Franz 2018). An increasing amount of research has appeared in the last year (e.g. Acarer 2023, Altunışık 2023, Huan et al. 2023, Muhib et al. 2023, Nacaratte et al. 2023, Taheri et al. 2023). In addition to identifying microplastics, factors that could affect the number of particles in the water were also investigated (Taheri et al. 2023). Researchers who have taken up this topic have indicated in their works that there are no standardized or unified methods for the sampling, preparation, and analysis of MP in drinking water, which makes it difficult or impossible to compare results (e.g. Kirstein et al. 2021, Stelmach & Aleksander-Kwaterczak 2023).

The aim of the work is to examine the content of solid particles, including microplastics, in bottled water from selected producers and available in Polish stores. The second aspect is predetermining whether exposing the same water bottles to various thermal and light factors will result in different particle content.

MATERIALS AND METHODS

Materials

Plastic bottled waters from different manufacturers were selected to assess their extraneous solid content, including plastic particles. The selection was made based on data about the waters most frequently purchased by consumers, i.e. the amount of water sold in stores. This decision was made in order to avoid the situation of waters that had been stored in a shop or warehouse for too long. The second criterion was to choose water in bottles made of a similar material – plastic of similar thickness, opacity, and colour (light blue), i.e. transmitting light to a very similar extent. Both noncarbonated and sparkling waters were selected from three different producers. Two bottles of water with a volume of 1.5 L were taken as

a representative amount – a sample – which gave 3 L of water to be analysed. Based on previously performed tests, it was found that the amount of 3 L is optimal as it allows enough particles to be obtained for further analysis. Every subsequent litre is a high risk of the overlapping of various particles, which makes their observation and identification difficult.

Table 1
Types of water used for research

Sample no.	Type of water	Mineralization	Main ingredients	Water treatment processes	Colour of bottle	Colour of bottle cap
1	non-carbonated	moderately mineralized (644 mg/L)	Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, F^{-}, HCO^{3-}, low-sodium	filtration and aeration	transparent, light blue	blue
2						
3						
4						
2		moderately mineralized (657 mg/L)	Ca^{2+}, Mg^{2+}, K^{+}, HCO^{3-}, low-sodium	filtration and aeration		blue
6		low mineralized (318 mg/L)	Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, F^{-}, HCO^{3-}, low-sodium	filtration and aeration		white
7		low mineralized (420 mg/L)	Ca^{2+}, Mg^{2+}, F^{-}, HCO^{3-}, low-sodium	filtration and aeration		orange
8		low mineralized (213 mg/L)	Ca^{2+}, Mg^{2+}, F^{-}, HCO^{3-}, low-sodium	aeration and ozonation		blue
9	sparkling	highly mineralized (1719 mg/L); content of CO_2: >4000 mg/L	Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO^{3-}, SO_4^{2-}, Cl^{-}	filtration and aeration		white
10		highly mineralized (1954 mg/L); content of CO_2: 1500 mg/L	Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO^{3-}, SO_4^{2-}, Cl^{-}, F^{-}	filtration and aeration, partial degassing		white
11		moderately mineralized (742 mg/L); high content of CO_2	Ca^{2+}, Mg^{2+}, HCO^{3-}, SiO_2 low-sodium	filtration and aeration		light grey

Methods

Most of the water samples were analysed immediately after purchase, with only an additional four samples from the same producer being exposed to controlled, different thermal and light conditions for two months, i.e.:

A – room conditions, temperature 22°C (±1°C),
B – fridge, temperature 5°C (±1°C),
C – near a heater, temperature 32°C (±1°C),
D – without access to light, temperature 21°C (±1°C).

After the specified time, all water samples were filtered using a filtration apparatus with a vacuum system and glass filters with a diameter of 47 mm and a mesh size of 1.6 μm (Merck Millipore) (Fig. 1). They were allowed to dry in glass Petri dishes, covered with perforated aluminium foil at room temperature.

After drying, the filters were observed under a Carl Zeiss Axio Imager.A1m (Series No. 3519001408) optical microscope in reflected white light at 10× or 20× magnification for retained solid particles of external origin. This was documented with photos using AxioVision (Zeiss). The visual way of counting particles may be subject to mistakes to a greater or lesser extent. Therefore,

particles so fine that they could not be counted accurately at the ten-fold or even twenty-fold magnification were omitted. The number of particles that was observed and counted during the microscopic observation of the entire glass filter is presented by division into shapes and colours and for two fractions. The particles were divided into those above and below 20 μm. This value was established indicatively because MP particles much smaller than the others were observed for this size. The results were calculated into the number of particles per one litre of water to make it easier to refer to the results published in other articles on this subject.

It was also occasionally a problem to determine the colour of the particle, which changed slightly with the change of focus or zoom. There is also the possibility that photos taken in graphics programs do not reflect the actual colour observed under a microscope, which is why some images may differ from the signature.

Subsequently, the composition of particles was analysed using FT-IR method. For each sample, specific particles were selected – due to the very large number, particles with the same shape and colour were not analysed. Measurements were performed directly on the filter. On this basis, all particles were divided into microplastics and other solid particles. FT-IR measurements were performed at National Synchrotron Radiation Centre SOLARIS using a Bruker Vertex80v spectrometer coupled with a Hyperion 3000 microscope equipped with a 64 × 64 element FPA MCT array detector.

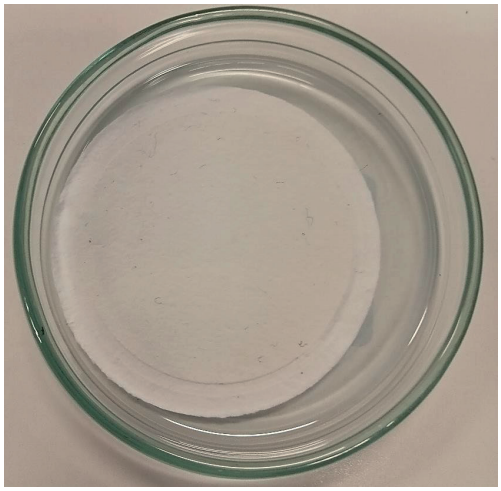

Fig. 1. *Glass filter used for water filtration after drying with visible particles*

IR spectra were collected with an ATR German objective (20×, numerical aperture 0.6, refractive index 4). Data acquisition was done in the 4000–700 cm^{-1} spectral range, with 4 cm^{-1} spectral resolution. For better illustration of the spectra, the correction of ATR intensity, smoothing, averaging of spectra, and background correction were performed.

The spectral range from about 1500 cm^{-1} to 500 cm^{-1} is called the "fingerprint" region. This part of the infrared spectrum is almost unique for any given material. The characteristic for polymer bands from CH_2 and CH_3 stretching vibrations can be found in the 3000–2800 cm^{-1} range. The assignments of major main peaks in polymer spectra are collected in Table 2. Various types of bending vibrations and carbon-carbon multiple bonds are not presented due to the multitude of functional groups and potential combinations in the polymer spectra.

Table 2
The main characteristic organic bands of polymeric materials (acc. to Veerasingam et al. 2020)

Wavenumber [cm^{-1}]	Vibration, functional group
2962 ±10	CH_3 asymmetric stretching
2872 ±10	CH_3 symmetric stretching
2926 ±10	CH_2 asymmetric stretching
2856 ±10	CH_2 symmetric stretching
1300–1100	C–O stretching
1750–1600	C=O stretching
3350 ±50	O–H stretching
1650, 1410	aromatic ring modes

Quality assurance and quality control

Recommendations published by Miller et al. (2021) were used to ensure the quality of the results. Optimum purity conditions were used for all analyses to avoid sample contamination by MP and other extraneous particles. Plastic tools and containers were not used during the experiments. They were replaced with glass or metal tools and containers with high resistance to abrasion. All of the equipment used was thoroughly rinsed with deionized water prior to use. Glass filters were used for filtration. During drying, the samples were covered with perforated aluminium foil to avoid the atmospheric deposition of particles.

Appropriate protective clothing and gloves were used while performing the analyses. During the FT-IR ATR measurements, the germanium crystal was cleaned before each measurement with a disposable lint-free wipe soaked in acetone. The measurement was made after the evaporation of the solvent.

Multiple counts and replicates of analysis were performed, and for more accurate counting, the filter was divided into 4–5 smaller fragments. Four blank samples were analysed simultaneously with the actual samples. Throughout the FT-IR ATR analyses sample spectra were co-averaged 64 times and background measurements (air) were performed at the same settings.

RESULTS

All of the samples on glass filters were visually assessed. On some filters, impurities were visible even to the naked eye (Fig. 1). Microscopic analysis showed the presence of some particles in all samples. All the results obtained in the first stage of the research are presented in the tables below (Tables 3, 4). The number of particles per litre of water ranged from 87 to about 188; on average, there were 136 ±32 particles in one litre of water. Particles smaller than 20 μm predominated in most of the samples (Table 3). There were from 0.0 to 2.0 particles per litre in blank samples and all of them were below 20 μm.

Table 3
Number of particles in samples of bottled water

Sample no.	Fraction [μm]	Fibres		Fragments		Granules		SUM		
								[%]	[pcs/3 L]	[pcs/L]*
1	≤20	0	*150***	72	*89*	21	*22*	35.6	261	87
	>20	150		17		1		64.4		
2	≤20	0	*108*	120	*162*	39	*48*	50.0	318	106
	>20	108		42		9		50.0		
3	≤20	0	*129*	171	*222*	43	*53*	53.0	404	135
	>20	129		51		10		47.0		
4	≤20	0	*112*	70	*145*	37	*40*	36.0	297	99
	>20	112		75		3		64.0		
5	≤20	0	*144*	186	*229*	41	*41*	54.8	414	138
	>20	144		43		0		45.2		
6	≤20	0	*143*	122	*162*	26	*26*	44.7	331	110
	>20	143		40		0		55.3		
7	≤20	0	*180*	244	*281*	26	*26*	55.4	487	162
	>20	180		37		0		44.6		
8	≤20	0	*232*	269	*298*	23	*35*	51.7	565	188
	>20	232		29		12		48.3		
9	≤20	0	*190*	195	*221*	31	*35*	50.7	446	149
	>20	190		26		4		49.3		
10	≤20	0	*128*	289	*318*	15	*21*	65.1	467	156
	>20	128		29		6		34.9		
11	≤20	0	*170*	255	*298*	16	*20*	55.5	488	163
	>20	170		43		4		44.5		
Minimum		–	108	–	89	–	20	–	261	87
Maximum			232		318		53		565	188
Arithmetic average			153		220		33		407	136
Median			144		222		35		414	138
Standard deviation			37		74		11		95	32

* Values rounded to the nearest whole number.

** The sum of particles in both fractions was marked with italics.

Shape

The observed particles were classified into three groups according to their shape: (1) fibres, (2) fragments, (3) spherical (granules). Fibres are elongated particles with a much smaller diameter than length (e.g. Fig. 2A, B). The fragments include irregularly shaped MP, films, foams, flakes, and foils (e.g. Fig. 2C, D), which are often treated separately in the literature, but due to difficulties in accurately distinguishing them, they were treated together. Granules particles have a regular and spherical shape (e.g. Fig. 2E, F).

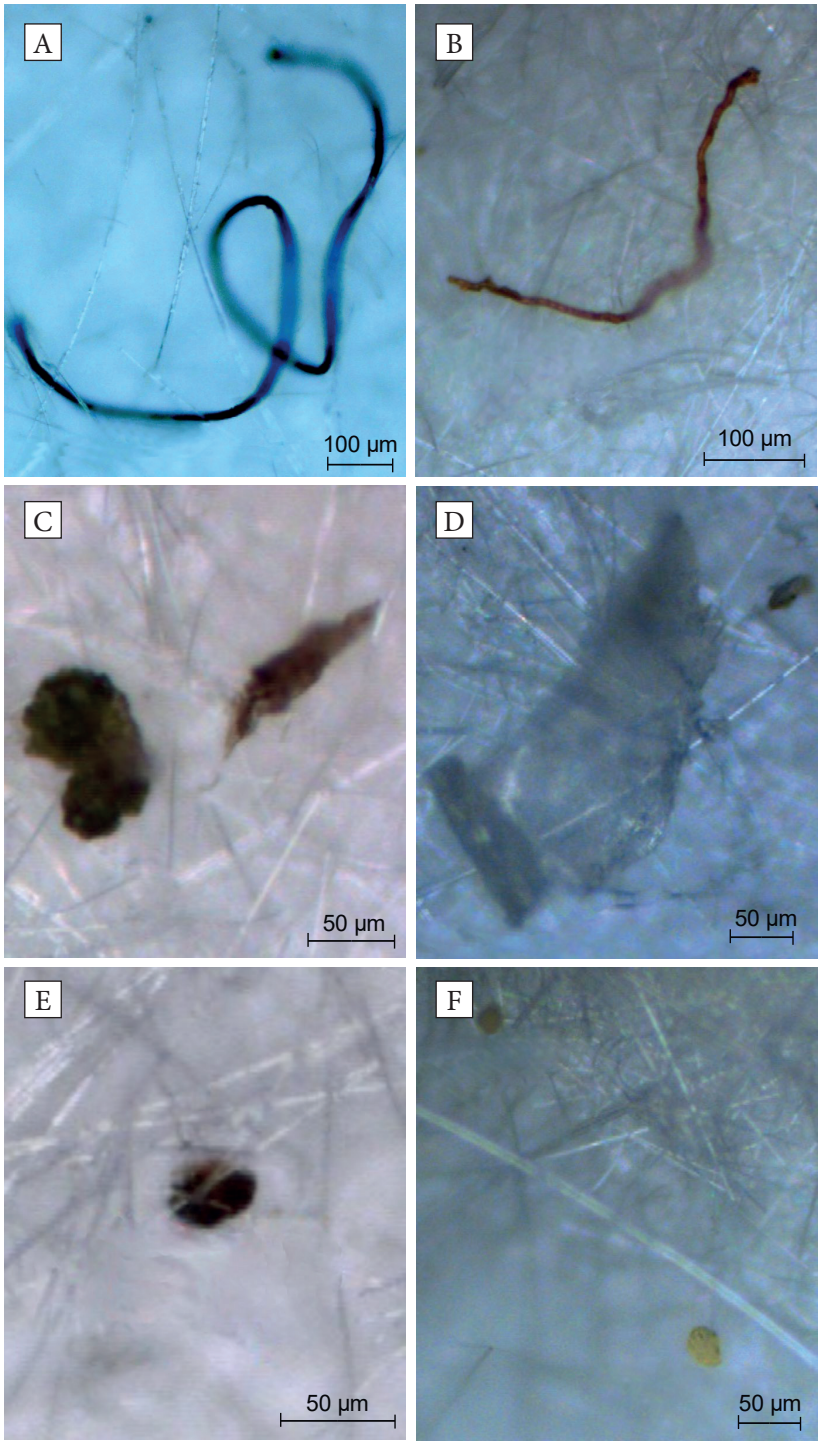

Fig. 2. *Shapes of particles separated from bottled water: fibre-shaped (A, B), fragments-shaped (C, D), and spherical-shaped (E, F)*

In terms of shape, the smallest number of spherical particles (8%) and the largest number of fragments (54%) were recorded in all samples, except for sample no. 1, where fibres predominated (Table 3). In the presented size range, where the limit was 20 μm, the fibre-shaped forms of particles in all samples had a longer length than the mentioned limit, with most being between 200 and 1500 μm long. On the other hand, fragments and spherical particles predominated in sizes smaller than 20 μm (Table 3). In ten samples, fragments of this size ranged from 74% to 90%. Spherical particles with a diameter <20 μm predominated in all samples, and their percentage ranged from 66% to 100%. The longest fibres that were observed on the filters were already visible to the naked eye, then at 2.5× magnification, several of them were visible at a short distance from each other (e.g. Fig. 3A, B). The largest number of fibres was recorded in sample no. 8 – 77 pcs/L, and the least in samples no. 2 and 4, where there were 36 pcs/L and 37 pcs/L, respectively (Tab. 2). The form of the fibres was different, e.g. close to a straight line or slightly wavy (e.g. Fig. 4A, B), twisted (e.g. Fig. 4C, D) or bunched (e.g. Fig. 4F, G). The length of the coiled fibres was difficult to determine. It is also possible that there were more fibres tangled together in such a bundle. The state of the fibres also varied, e.g. smooth and compact (e.g. Fig. 5A, B) or ragged and stratified (e.g. Fig. 5C, D), which may show a tendency to further disintegration. Fibres with a circular or flat cross-section predominated.

Considering the shapes of fragments, there was considerable variation. Fragments (e.g. Fig. 6A, B) including films (e.g. Figs. 2D, 6C, D) and flakes (e.g. Fig. 6E, F) with irregular edges have been observed. A visible feature of the foil is its certain transparency. The largest number of fragments was observed in sample no. 10 – 106 pcs/L. It was also characterized by the highest percentage (91%) of particles below 20 μm (Table 3). The fewest fragments were found in sample no. 1 – 30 pcs/L. The smallest percentage share of particles below 20 μm was found in sample no. 4 and amounted to 48%. The size range of these particles was extensive, i.e. from less than 10 μm (e.g. Fig. 6G, H) to about 500 μm (e.g. Fig. 6D). The vast majority of particles were flat, but some clearly had a third dimension, i.e. thickness (e.g. Fig. 6I). Among the fragments, those with a size below 20 μm predominated.

Spherical particles are the most regular shaped ones among particles. In all the analysed samples, such particles were the smallest, only 8% (Table 3). In samples no. 1, 10 and 11, the least particles were recorded – only 7 pcs/L, and the maximum in samples no. 2 and 3 – 16 pcs/L and 18 pcs/L, respectively.

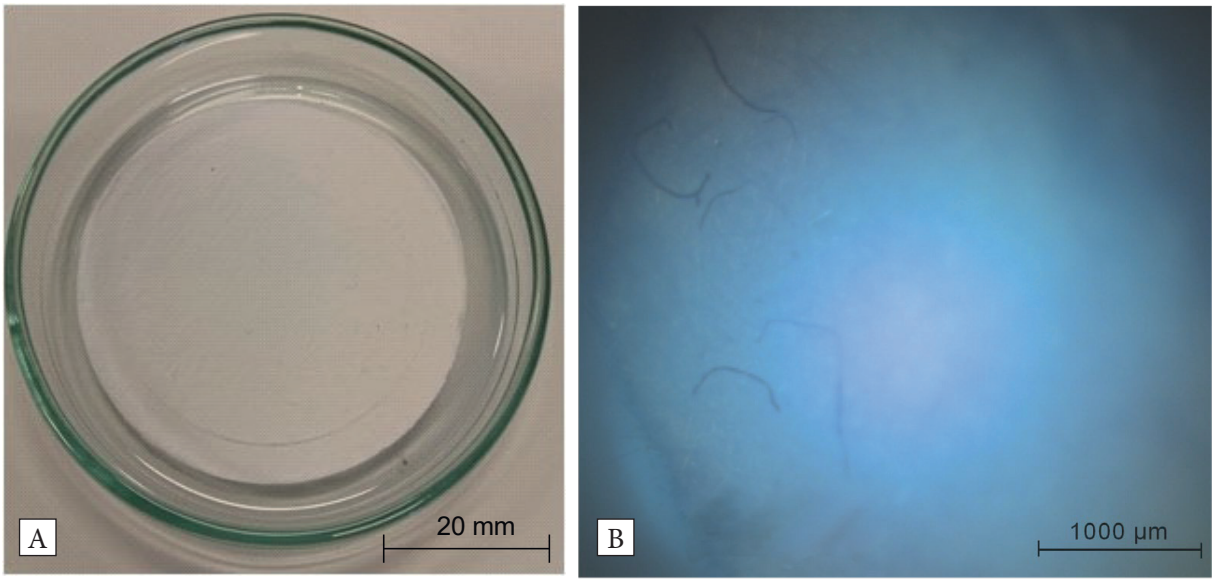

Fig. 3. *Fibres visible to the naked eye (A) and under the microscope at 2.5 times magnification (B)*

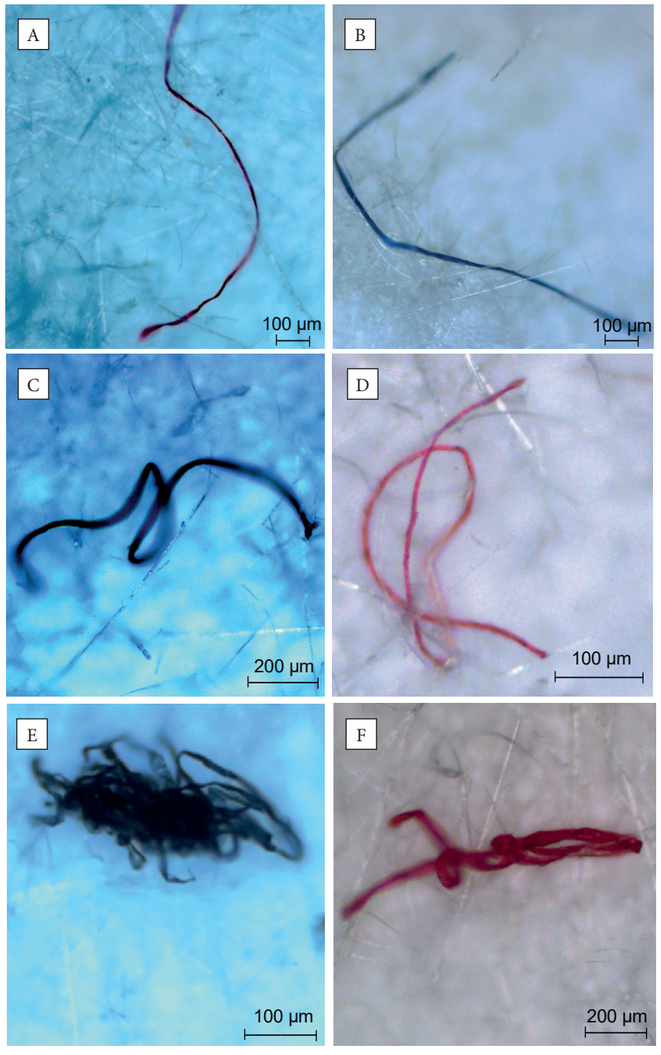

Fig. 4. *Forms of fibres: straight/slightly waved (A, B), twisted (C, D), and bunched (E, F)*

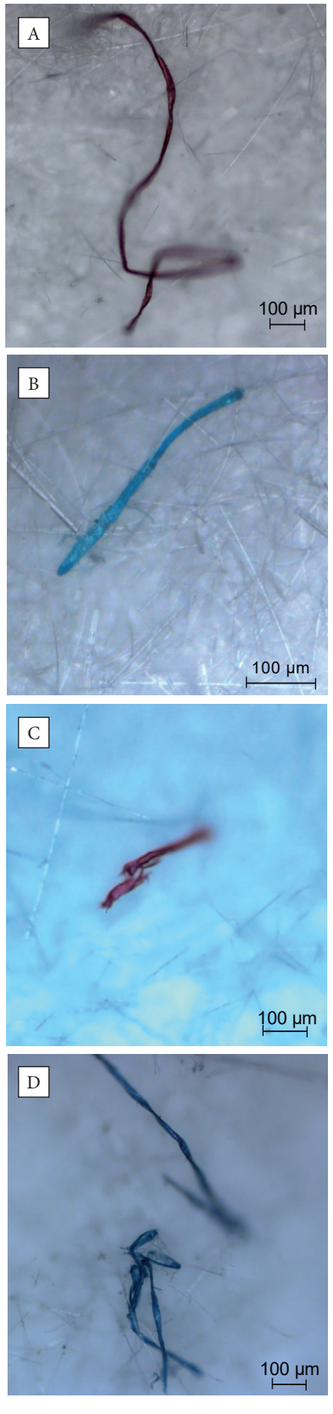

Fig. 5. *The state of the fibres: smooth and compact fibres (A, B), delaminate (C, D)*

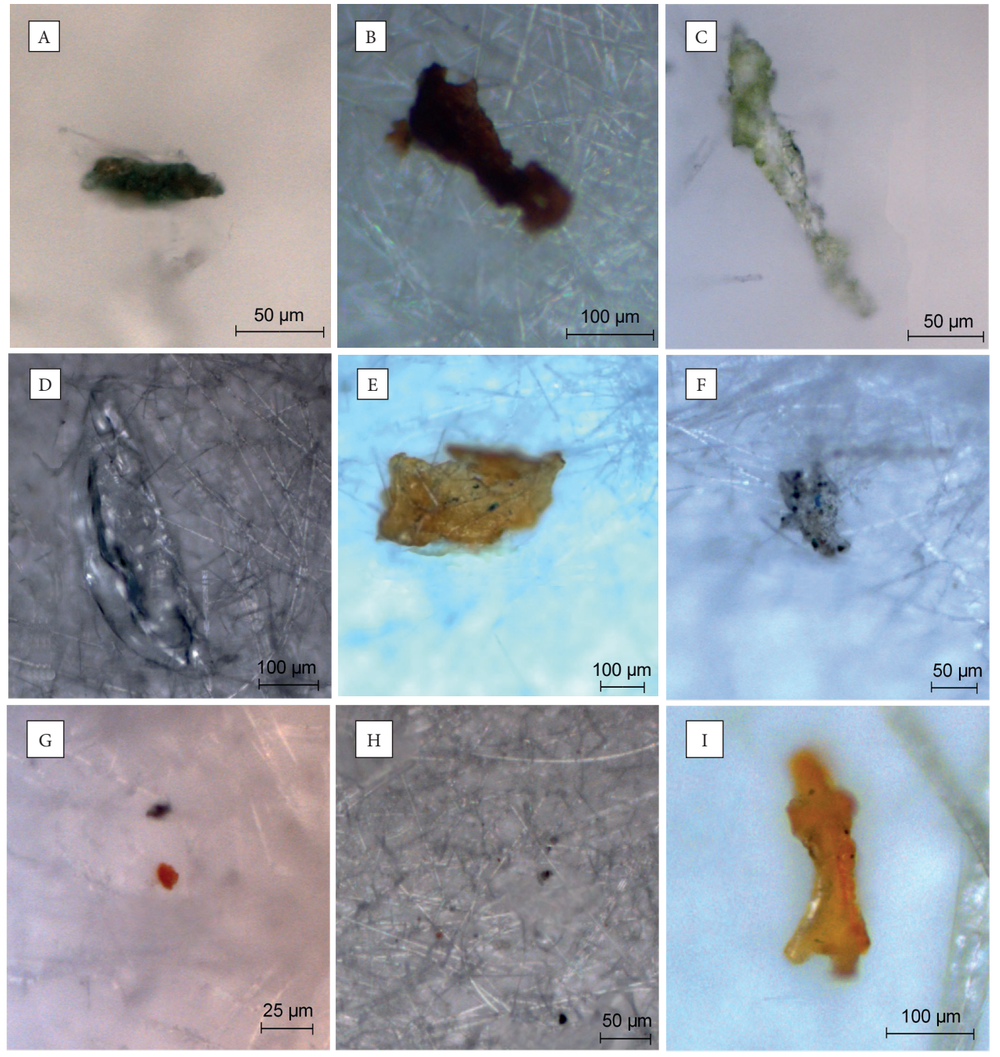

Fig. 6. *Forms of particles counted as fragments: typical fragments (A, B), films (C, D), flakes (E, F), smallest fragment (G, H), and a fragment much thicker than the others (I)*

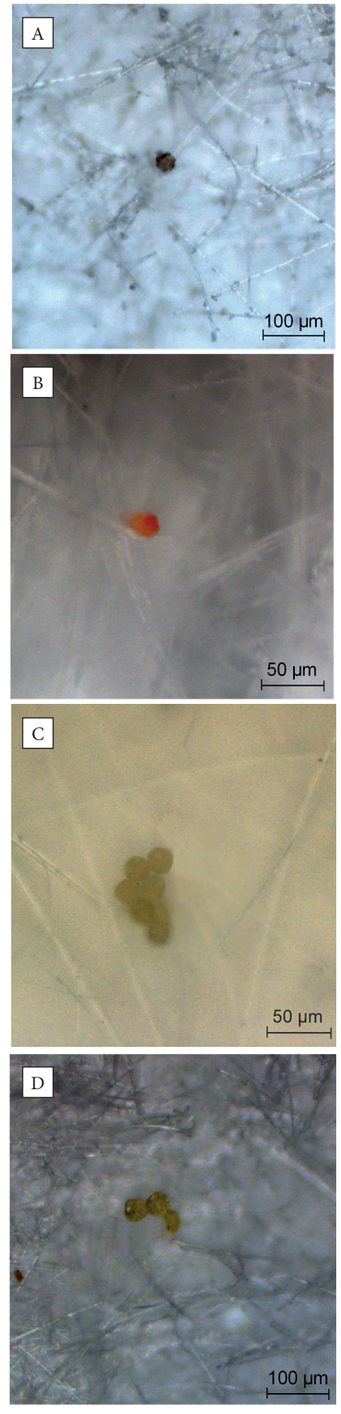

Fig. 7. *Spherical forms of particles: shape close to spherical (A, B), perfectly round shape (C, D)*

The number of particles below 20 µm was significantly greater than above 20 µm. No spherical particles larger than 20 µm were observed in samples no. 5–7. The percentage of particles <20 µm was 66–100%. The size of the spherical particles observed in the samples was ca. 10–40 µm. Most had a shape close to spherical (e.g. Fig. 7A, B), but a few were found in gold with a perfect round shape. In sample no. 8 they were concentrated close to each other, touching in the number of 7 particles with a diameter of approx. 20 µm, and in sample no. 11 – 3 (one was slightly deformed) with the same diameter (e.g. Fig. 6C, D).

Colours

The colour of the particles that predominated among the tested samples was a very light blue (almost colourless). The fewest particles were observed in the colours: orange, pink and yellow, only a few or a dozen in all samples. Taking into account the number of particles of a given colour, brown, black, blue, gold, red, green, and turquoise were found right after the colourless ones. This order resulted from the summation of all particles in individual colours, in specific cases it differed slightly from this order (Table 4).

Table 4
Shapes and colour of particles in bottled water (pcs/3 L)

Sample no.	Shape	FIBRES											SUM	
	Colour	black	brown	colourless	red	blue	green	turquoise	yellow	orange	pink	gold		
1		61	5	36	15	23	9	0	1	0	0	0	150	
2		20	6	67	4	6	2	2	1	0	0	0	108	
3		47	0	42	17	14	2	3	3	0	1	0	129	
4		17	7	73	3	12	0	0	0	0	0	0	112	
5		13	5	98	14	9	3	0	0	0	1	1	144	
6		29	4	65	2	40	2	1	0	0	0	0	143	1686
7		23	3	124	5	13	4	1	0	0	0	7	180	
8		17	1	195	4	9	6	0	0	0	0	0	232	
9		26	8	126	5	21	0	3	0	0	0	1	190	
10		21	3	91	2	7	3	1	0	0	0	0	128	
11		16	1	140	2	9	0	0	0	0	0	2	170	
Sample no.	Shape	FRAGMENTS											SUM	
	Colour	black	brown	colourless	red	blue	green	turquoise	yellow	orange	pink	gold		
1		19	41	18	2	4	2	0	3	0	0	0	89	
2		33	49	73	0	3	2	1	0	0	1	0	162	
3		40	77	92	1	3	3	5	0	1	0	0	222	
4		15	39	79	3	7	2	0	0	0	0	0	145	
5		30	79	111	2	3	3	0	0	0	0	1	229	
6		25	39	91	3	2	2	0	0	0	0	0	162	2425
7		47	67	158	1	3	3	0	0	0	0	3	281	
8		54	80	154	2	3	1	0	0	0	0	4	298	
9		29	83	89	2	1	1	1	0	0	0	15	221	
10		50	90	165	0	3	3	0	0	0	0	7	318	
11		40	108	138	0	3	2	2	0	0	0	5	298	

Table 4 *cont.*

Sample no.	Shape	GRANULES											SUM	
	Colour	black	brown	colourless	red	blue	green	turquoise	yellow	orange	pink	gold		
1		13	4	0	2	1	0	1	1	0	0	0	22	
2		14	21	6	2	0	2	0	2	0	1	0	48	
3		27	18	6	1	1	0	0	0	0	0	0	53	
4		11	23	6	0	0	0	0	0	0	0	0	40	
5		15	18	7	0	1	0	0	0	0	0	0	41	
6		16	7	2	0	1	0	0	0	0	0	0	26	367
7		7	9	4	0	0	0	0	0	1	0	5	26	
8		12	9	1	0	0	0	0	0	0	0	13	35	
9		8	7	3	0	1	0	0	0	0	0	16	35	
10		5	5	3	0	0	0	0	0	0	0	8	21	
11		4	4	3	0	0	0	0	0	0	0	9	20	

The most colourless fibres were found in sample no. 8 – 65 pcs/L (Table 4), and the least in no. 1 and 3 – 12 pcs/L and 14 pcs/L, respectively (e.g. Fig. 8A–C), in which black fibres dominated (e.g. Fig. 8D–F). Although the brown colour ranked second in the total number of particles, it was less prevalent among the fibres (e.g. Fig. 8G, H), because mainly black, red (e.g. Fig. 8I) and blue (e.g. Fig. 8J) fibres appeared there. Sample no. 6 was distinguished by a large share of blue fibres compared to the other samples. Multicoloured fibres (e.g. Fig. 9A) or those faded along part of their length (e.g. Fig. 9B, C) were also noted.

The share of individual colours among the fragments was different than for the fibres; colourless dominated, followed by brown, black, blue, gold, green, and red. The most colourless fragments were in sample no. 10 – 55 pcs/L (e.g. Fig. 10A, B, Table 4), brown in sample no. 11 – 36 pcs/L (e.g. Fig. 10D–F), black in no. 8 – 18 pcs/L (e.g. Fig. 10H, I). Gold fragments prevailed in sample no. 9 – 5 pcs/L (e.g. Fig. 10C). There were several times fewer red (e.g. Fig. 10G) and blue (e.g. Fig. 10J) fragments than fibres in these colours. Some particles showed a heterogeneous colour, were "glossy" and dark spots could be seen in the centre (e.g. Fig. 11). According to their shapes, they were classified as flakes.

Spherical particles were the only shape in which black, brown, and gold colours were dominant, and not colourless as in other shapes. The other colours were represented by single particles. The largest number of black spherical particles was in sample no. 3 – 9 pcs/L (Table 4), brown ones in sample no. 4 – 8 pcs/L. Golden spherical particles were only noticed in samples no. 7 – 11 pcs/L, most of them in no. 9 – 5 pcs/L (e.g. Fig. 7C, D).

Identification of microplastics

The particles obtained from the filters were analysed by FT-IR microspectroscopy for the identification of microplastics. Particles of different shapes and colours were selected for the analysis for each sample. A total of 158 analyses were made. The results showed the presence of different kinds of polymers, both naturals and synthetic. The spectral profiles for each microplastic particle showed characteristic bands.

The obtained spectra showed low intensity, but the bands were well separated and it was easy to discriminate between them. Cellulose predominated among all of the polymers (approx. 30%). Taking only MP into account, polyvinyl chloride (PVC) particles (approx. 50%) and polyamide (PA) (approx. 30%) were the most numerous. The other particles are polyethylene terephthalate (PET), poly(buthadiene), polymethyl methacrylate (PMMA), polystyrene (PS), polyethylene (PE), and polypropylene (PP). In many cases, the signal was too weak to assign the polymer to a specific group.

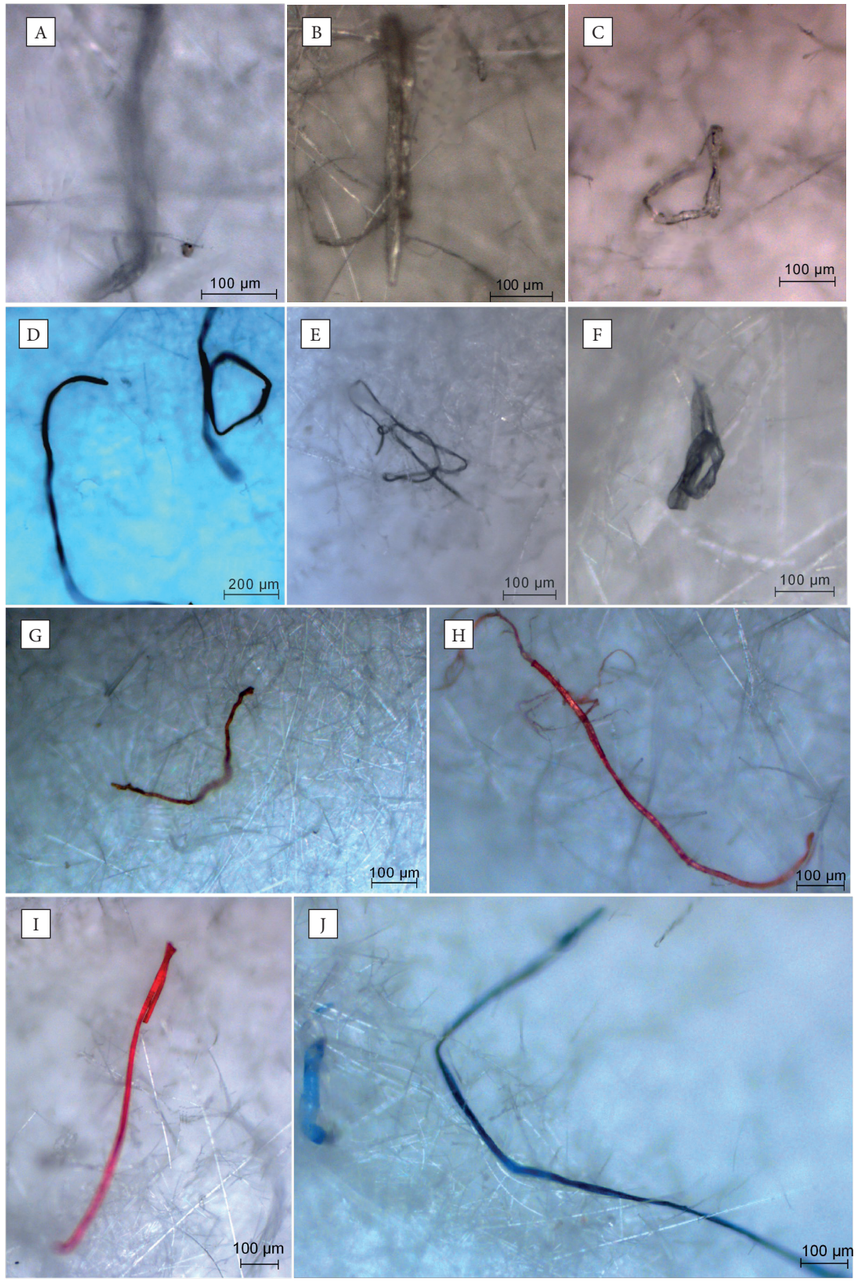

Fig. 8. *Colours of fibres in water samples: colourless (A–C), black (D–F), brown (G, H), red (I), and blue (J)*

Fig. 9. *Multi-coloured fibres (A) or partially faded fibres (B, C)*

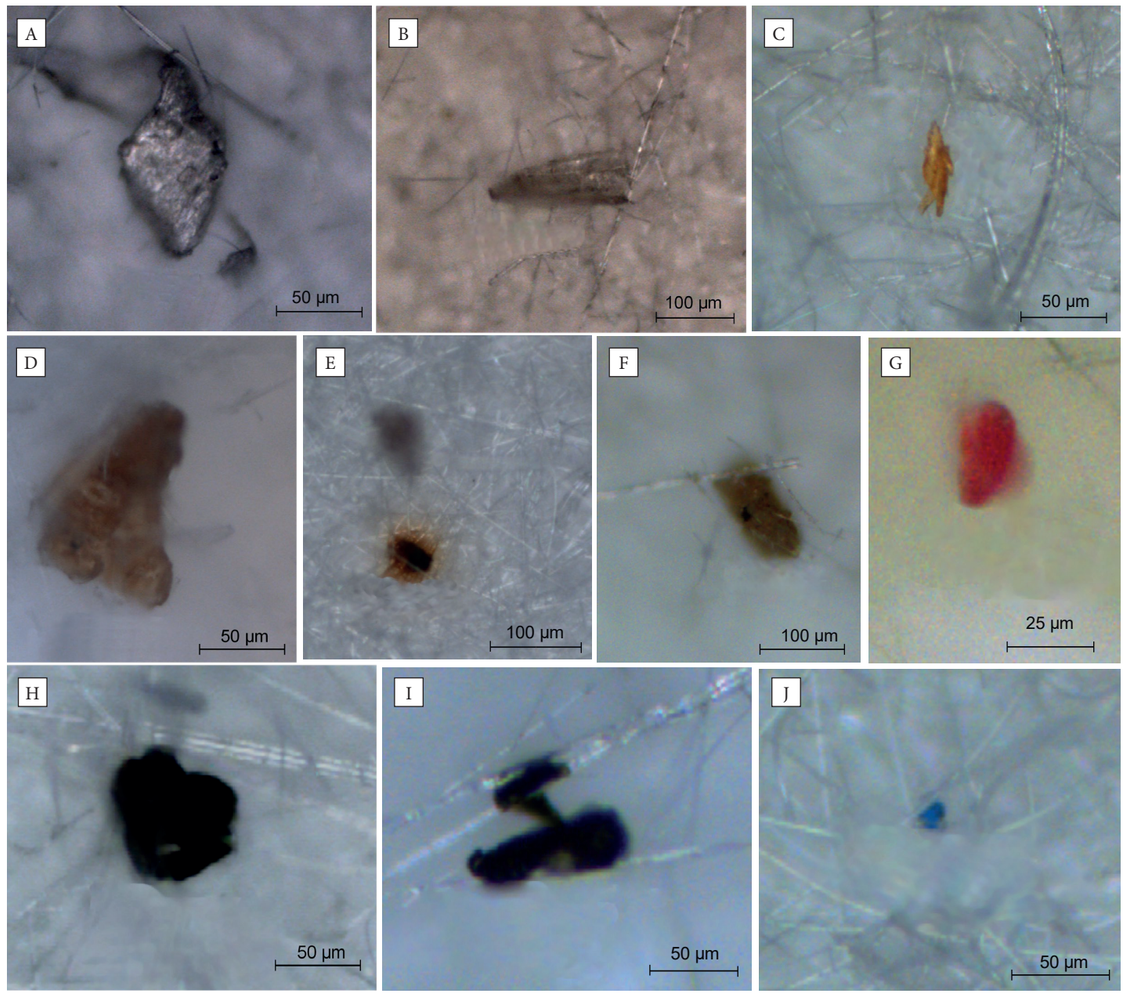

Fig. 10. *Colours of fragments: colourless (A, B), gold (C), brown (D–F), red (G), black (H, I), blue (J)*

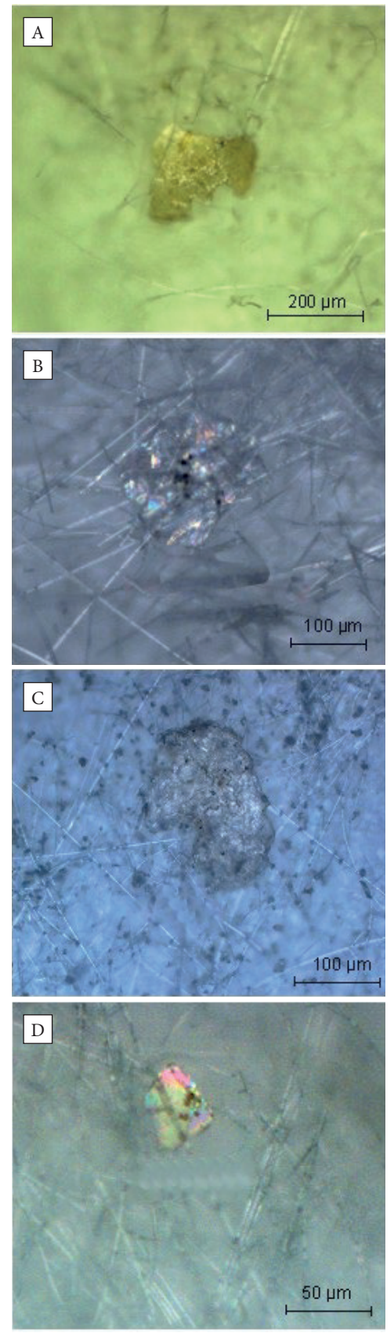

Fig. 11. *"Glossy" golden and colourless particles with dark spots in the centre in samples*

Figure 12 shows two exemplary dominant spectra – for a natural polymer (Fig. 12A) and a synthetic one (Fig. 12B).

At Figure 12A the O–H stretching band at 3336 cm^{-1} is about 700 cm^{-1} wide at the base. Also, the characteristic bands of functional groups can be found: C–O stretching bands between 1300–1000 cm^{-1}. Other peaks are at 1461 cm^{-1} (CH_2 bending), and 1313 cm^{-1} (OH rocking with CH wagging). Based on the spectra (Zhang et al. 2010), it can be concluded that the microplastics belong to the polysaccharide type, most likely being cellulose.

Two very characteristic bands at positions 1650 cm^{-1} (C=O stretching) and 1642 cm^{-1} (N–H bending) in Figure 12B indicate that the MP belongs to the group of nitrogen polymers. The band at 3278 cm^{-1} can be assigned to N–H bending vibration, and at 1037 cm^{-1} to C–O stretching. The presence of a high-intensity C–O band suggests that the polymer belongs to the group of polyurethanes (Asefnejad et al. 2011). Otherwise, in the absence of broad bands, one may suspect that the molecule belongs to the polyamide group. Particularly interesting is the fact that all of the spectra show the presence of functional groups and only some of them can be attributed to the most popular thermoplastics: polypropylene, polyethylene, and polyethylene terephthalate.

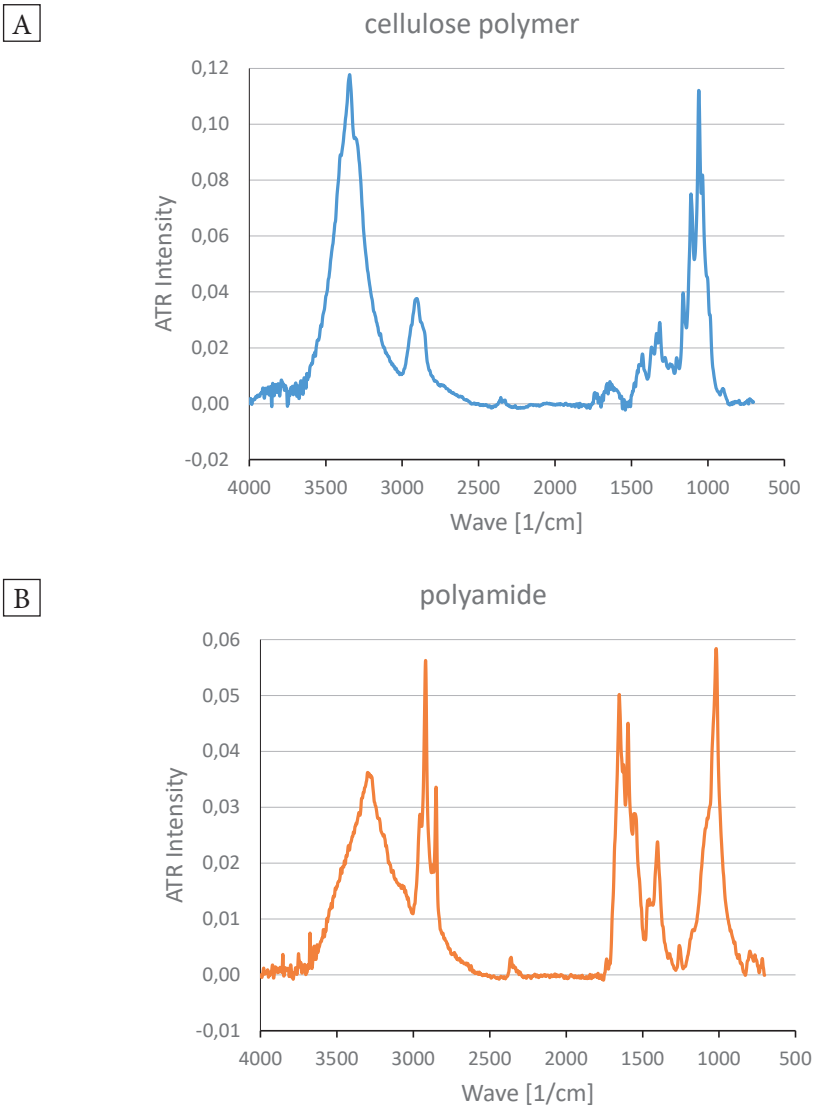

Fig. 12. *Spectra of some of the polymer particles (IF-IR, ATR) in bottled waters*

DISCUSSION

Influence of particle size on results

Samples of bottled water were analysed by filtration and microscopic observation for the presence of extraneous particles and FT-IR spectroscopy analysis to confirm or negate whether the separated particles were microplastics. Microscopic observation allowed precise counting of particles larger than 10 μm. Smaller particles were difficult to see (even at 20× magnification) or difficult to count because they were abundant and/or very close together. Therefore, the range of microscopic analysis was from approx. 10 μm to over 1500 μm. The pore size of the filters used in the study was 1.6 μm, which means that particles from this size to approx. 10 μm that remained on the filter were not included in the total number of particles, i.e. the result may be underestimated. In this work, the particles were divided into those above and below 20 μm (Table 3). Particles smaller than 20 μm were from about 35 to 65% of the sample. Similarly, as in the case of other researchers (e.g. Mason et al. 2018, Oβmann et al. 2018, Schymanski et al. 2018), it was confirmed that most of the particles are of the smallest size, but depending on the research, this limit was different. The number of MP particles detected in the studies of these researchers differs significantly.

In general, comparing the results of available studies on MP in bottled water is difficult due to the different methods of sampling, preparation, and counting (Taheri et al. 2023). For example, Schymanski et al. (2018) used filters with a surface area of approx. 12.6 mm^2 during water filtration and samples with a volume of 0.7–1.5 L, and micro-Raman spectroscopy to identify particles. Oβmann et al. (2018) dissolved the calcium and magnesium carbonates present in the water before filtration and the sample volume was reduced to 250 mL. The identification of MP particles was carried out point-wise, i.e. five places with an area of 1 mm^2 each were selected, which accounted for 4.4% of the entire filter surface, i.e. 113 mm^2. Particles from these sites were analysed by micro-Raman spectrometry. The possibility of analysing particles down to the size of 1 μm resulted in a much larger number of them – compared to the studies of Schymanski et al. (2018). In addition, the results of Oβmann et al. (2018) are not a real number, but an estimate based on the number of particles from an area of 5 mm^2. That extrapolation increases the uncertainty of the results, and the method of converting the number of particles by taking into account the filter area and the volume of water could lead to overestimation (Welle & Franz 2018). In the case of the research of Mason et al. (2018), Nile Red was added to the water before filtering. This is absorbed by the surface of plastics, while most natural materials are not, and makes it possible to count them. Their morphology was then examined and part of them was analysed by FT-IR spectroscopy, i.e. using infrared to confirm whether they are plastic particles. This method allowed the identification of particles above 6.5 μm, because this was the resolution of the images. The advantage of Raman spectroscopy is that it is able to analyse particles smaller than FT-IR spectroscopy but the intensity of the laser may destroy them before results are obtained (Mason et al. 2018, Welle & Franz 2018). A great facilitation is the Nile Red application, which can be used for the rapid detection of MP without the need for additional spectroscopic analysis (Erni-Cassola et al. 2017, Maes et al. 2017, Meyers et al. 2022, Shruti et al. 2022). However, it does not give information about which polymer we are dealing with.

Analysing all of the data, it can be observed that bottled waters contain the most MP particles of smaller sizes. This leads to the conclusion that the ability to analyse fine particles gives a broader picture of MP content in bottled waters. Such information may be important in the analysis of microplastics in terms of health risks. The predominance of smaller particles can be explained by the water being subjected to various treatment processes before being bottled and preventing larger fragments from being included. An interesting aspect raised by WHO (2019) is the impact of aerobic processes on MP status, such as ozonation, chlorination, or advanced oxidation used in water treatment. All other substances are affected by these processes, so there is no reason to believe that they do not affect MP, but it is poorly understood whether this only affects the surface of MP

or if they can cause further fragmentation of particles into smaller fragments.

Shapes and colours of particles

In the study, the particles were divided in terms of shape into three groups: fibres, fragments, and spherical particles. The percentage share was as follows: fragments – 54%, fibres – 38%, spherical particles – 8%. The only particles that were visible to the naked eye on the filters were fibres, as some of them were 1 mm or more in length. The group of fragments included all irregular particles, films, foams, flakes, and foils, because the visual method of their identification did not allow for their more precise assignment. Most of them were flat, but one was found that was distinguished by rounded outlines (Fig. 6I). It may have been a particle with a greater thickness than the others, or its arrangement/collapse caused it to look that way under the microscope. Among the spherical particles observed, only a few were perfectly round (Fig. 7C, D) and all were golden. This shape suggests that they are primary MP and may come from cosmetics.

Mason et al. (2018) also characterized the morphology of MP particles in their work. Fragments (65%), films (14%) and fibres (13%) predominated, and grits accounted for 3%. It is difficult to compare these data with those obtained from the study, as they only refer to particles >100 μm. However, the general conclusion is the same, i.e. in terms of shape, fragments are the most numerous and constitute more than 50%, and shot, i.e. spherical particles, is the least numerous, at several percent. This distribution can be explained by the fact that round particles (e.g. shot) are not often found in nature. They are mostly primary MP, i.e. deliberately produced in such a shape, and the size indicates their origin as being cosmetics (Cowger et al. 2020). The fragments come from the breakdown of larger products or plastic waste, so they are irregular. In addition to those that were already in the water taken from the source, they may also come from the bottling process and from the degradation of the packaging itself. Fibre-shaped microplastics primarily enter water from the deterioration of clothing and carpets, while in bottled water they are more likely to come from airborne particles or those of smaller sizes (mainly in diameter) could also occasionally get through during the filtration process. The shape of the particles may matter when talking about the effects of MP on the digestive system (or otherwise, when MP gets there). Irregular, sharp fragments can injure tissues, while fibres can dig into them.

The origin of particles in water can be determined on the basis of shapes, but a second source of such information can also be colour, although this is not so clear due to the variety of colours of plastics. In the study, colourless particles dominated, followed by brown, black and blue. Assuming the theory that a certain amount of MP particles may come from packaging, the advantage of colourless particles is justified, because the water for the tests came from colourless (light blue) bottles. Most of the particles were single-coloured, but there were multi-coloured or partially faded particles, and even shiny, non-uniform with black dots in the centre. The particles may have faded due to light exposure, suggesting their long presence in the environment, or chemical factors that may affect the environment. The image of shiny particles may be due to light falling on them, but these black spots may also be, for example, pinholes or secondary precipitates. More detailed research is needed to verify this. If they were precipitations or accumulations of some material, it may be important in the case of research on the transport of various substances by MP, e.g. heavy metals, persistent organic compounds, chemical additives from the production process of the material from which they were formed. After getting into the digestive system, these substances can be released and have a negative effect on the body.

Not only is the colour of the bottle important, but so also is the cap. According to a study by Giese et al. (2021) and Singh (2021), repeated unscrewing and capping of the bottle results in the release of fragments of the cap, which may result in a greater number of MP particles in the colour of the cap with the repeated use of one bottle. Our research did not take into account the repeated closing and opening of bottles, and particles with a colour similar to the colour of the cap occurred sporadically. Hence, additional research should be conducted to confirm this.

Influence of conditions and environment on particle content

According to the data from 2021 about European plastic production, demand, and waste, the greatest demand is for polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), other thermoplastics, polyurethanes (PU) and polystyrene (PS) (PlasticsEurope 2021). In our study, during the preliminary analysis of the spectra, about 20% of them were rejected because various spectral disturbances appeared. They were most likely due to the presence of other particles, including the glass fibres from which the filter was made. They could also stem from unevenness on the surface of the filter, resulting from distortions during filtration. Based on the analysis of the remaining spectra, it was found that about 75% of them are polymers, and the rest various other particles. The results obtained confirm the presence of MP of various sizes, shapes, and colours. Particularly interesting is the fact that only some of them can be attributed to the most popular thermoplastics: PP, PE, and PET. However, the microplastic particles were partially degraded by atmospheric conditions, including water and ultraviolet radiation. Degradation and the accompanying chemical transformations distort the spectrum of polymers. There is also a very high probability that these materials might predominate in the smallest fractions which could not be identified with the method used.

Differences in the number of MP particles in waters from different producers were found and which may be related to several factors. These waters differ primarily in origin, which affects how they were prepared before bottling and what processes they were subjected to. Differentiating factors may also be the properties of the bottle, i.e. its thickness, strength or shape, as well as the production and bottling line as well as the length and/or conditions of storage, transport to the place of storage or sale of bottles (Campanale 2020, Yuan et al. 2022).

Generally, PET, which bottles are made of, and PP, which is most often used for caps, predominate among polymers (Mason et al. 2018, Oβmann et al. 2018, Schymanski et al. 2018, WHO 2019). Differences in the results regarding the content of MP may result from the different methodology employed and indicate, for example, that the particles, depending on the size, differ in the types of polymers that show varying degrees of resistance to fragmentation, e.g. due to different density.

Schymanski et al. (2018) indicate that not only the packaging and bottling process of water can affect the amount of MP in bottled water, but also what the water is like, i.e. whether the water is sparkling or not. In their study, they showed that there were more MP particles in carbonated water than in still or moderately carbonated water. In our study, the number of particles was similar in sparkling waters (sample 9–11), i.e. 149, 156, 163 pcs/L, respectively. These values were higher than the average (136 pcs/L) and higher than six samples (no. 1–6). More than 163 pcs/L were only recorded in one sample – 188 pcs/L (no. 8). Three samples are not enough to clearly state that carbonated water contains more MP particles than non-carbonated water, but it encourages further research in this direction.

Another aspect analysed in the conducted study was the comparison of the number of particles in water that was exposed to different thermal and light conditions for two months. Samples 1–4 were bottles from one manufacturer, purchased in the same store and at the same time, so there is a high probability that they are from the same batch (bottles from one case). The process of producing bottles and filling them with water is automated, so each piece is the same as the next. During storage and transport, they are subjected to the same actions, from which it can be concluded that, at the time of purchase, the level of water in each of the purchased bottles was the same. The purpose of the differentiation of the conditions was to check whether they would affect the amount of MP in the water. The highest number of particles was found in sample from bottles placed near the heater – 135 pcs/L (Table 2), which may indicate that higher temperatures increase the number of particles. While on a radiator is not a place where water bottles are kept, it was supposed to imitate conditions in which they are often found, e.g. in a hot car, on a sunny windowsill. The second in order was the sample from the refrigerator – 106 pcs/L and it was a result similar to the sample from the basement – 99 pcs/L. It can

be concluded that low temperatures may also result in a higher number of MP. The fewest particles were observed in sample no. 1 – 87 pcs/L, which was kept at room conditions, i.e. those in which such bottles are most often kept. If we consider the shape of the particles, the greatest number of fragments and spherical particles were found in the sample from the radiator, while fibres predominated in water stored at room temperature.

Tests of water in reusable plastic bottles show an even higher MP content in the water. This can be explained by the fact that the reusable bottle has been subjected to different factors (washing, refilling, transport, repeated unscrewing, pressure) more times than disposable bottles, which may lead to more MP particles, primarily PET (Mason et al. 2018, Welle & Franz 2018, Oβmann 2020). Giese et al. (2021) checked the effect of repeated unscrewing and screwing of a returnable plastic bottle on the number of MP particles. They used PET bottles with PP caps and PE seals. After the first unscrewing, Raman microscopy revealed 131 ±25 pcs/L, and after 11 times of unscrewing and screwing – 242 ±64 pcs/L. This change was caused by an increase in the number of PP particles from 100 ±27 to 185 ±52 pcs/L. The concentration of PET and PE particles did not increase significantly, indicating that these particles originated from the cap. Similar studies were obtained by Winkler et al. (2019), who found that PET bottlenecks and high-density PE caps are a serious source of PM, especially after prolonged mechanical stress (the opening and closing procedure).

The study conducted by Mason et al. (2018) was for water in both glass bottles and disposable PET bottles. MP was confirmed in 93% of the bottles. The researchers also confirmed that the dominant polymer among the MP found in water from plastic bottles is PET. In the case of water from glass bottles, PE and styrene butadiene copolymer predominated (Welle & Franz 2018). Kankanige & Babel (2020) also found MP in glass-bottled water (52 ±4 pcs/L). This may indicate the origin of plastic particles from sources other than the degradation of bottles and caps. In order to determine how many MP particles come from the bottling and packaging process, it would be necessary to test the water after taking it from the source, prior to bottling, and after purchase. This would show whether the groundwater, which is the main source of bottled water, is contaminated with these anthropogenic particles and to what extent the packaging affects their amount in the water.

Summary and guidelines

Taking into account the obvious fact that we cannot exist without water, and that the consumption of bottled water is increasing, it is necessary to implement very strict quality control procedures at every stage of its production and life cycle. The research of Altunışık (2023) has shown that long-term consumption of bottled water contaminated with MP can even pose a risk to human health. Therefore, we should also take care of its proper storage and use bottle closures that are not subject to mechanical damage, which leads to an increase in the number of plastic particles entering our bodies.

Considering the results obtained, the health aspects and the need to introduce requisite legal regulations should be encouraged. The lack of legal regulations in Poland was addressed to some extent in 2021 by the Supreme Audit Office in the document "Protection of people against the harmful effects of plastics" (NIK 2021). The State Sanitary Inspection did not include the impact of microplastics in drinking water on the life and health of consumers in its procedures, because it did not appear in the national catalogue of parameters for the determination in water intended for human consumption, which resulted from the fact that it was not included in the list of parameters of the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (Directive 1998) and was not indicated as a parameter required to establish additional protection of human health. The European Commission has until 2024 to establish research methodologies for testing the content of microplastics in drinking water in accordance with Directive of the European Parliament and of the Council of December 16, 2020 on the quality of water intended for human consumption (Directive 2020), which has been in force since January 2021.

The lack of official guidelines also applies to the conditions that should be met by laboratories

for MP analysis. Minimum requirements and best practices for MP analysis in drinking water including Raman spectroscopy and FT-IR were presented by Schymanski et al. (2021) and Miller et al. (2021). This applies to avoiding clothes and gloves made of artificial materials, minimizing the use of things made of plastic in the laboratory, e.g. water containers, controlling the air flow during filtration, and protecting the filters against the deposition of particles from the air, and analysing blank samples.

CONCLUSIONS

The analysis of the content of solid particles in bottled waters permit the conclusion that all of the analysed water samples from various producers contain some solid particles (87–188 pcs/L). This may indicate that water from disposable plastic bottles available in stores is contaminated with various substances. The difference between the highest and lowest particles content is almost 100 pcs/L. It may result from the origin of the waters, the processes they were subjected to prior to bottling, the properties of the bottles as packaging, and the conditions and length of storage and transport. Additional FT-IR analysis confirmed that about 75% of them are polymers, but it can be concluded that bottled waters contain the most MP particles of smaller sizes. This can be explained by the fact that the water is subjected to various treatment processes before being bottled and the larger fragments not being able to get there. Such particles can most easily be passed through inspection processes, and at the same time they can pose a risk to consumers.

In the study, the most particles were in the form of fragments (54%) and fibres (38%), with the least being spherical particles (8%). The domination of irregular shaped ones may indicate that they come from the destruction of waste or plastic products. The low share of spherical particles may be due to the fact that such regular shapes are rare in nature, and they mainly get into water from cosmetics and cleaning products. The dominant colour (over 50%) among the MP particles was very light blue (almost colourless), which may indicate that these particles can come from the destruction of bottles with such a colour.

More MP particles were found in waters exposed to high and low temperatures than in waters stored at room temperature, which may indicate that drinking water storage conditions are important. Information about proper water storage can be found on the labels of most bottled water sold in Poland but not everyone always reads them. The content of MP particles in carbonated water was one of the highest, which may mean that carbon dioxide dissolved in water affects the content of MP particles. It is also important to check the influence of aerobic processes, such as ozonation, chlorination or advanced oxidation used in water treatment on particle content in bottled waters. Taking into account the results obtained, the health aspects and the need to introduce the necessary legal regulations should definitely be considered. The lack of any legal guidelines or unified standards in the field of research on MP means that the results are not always representative, and it also makes it difficult to compare the results of different researchers.

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